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VI.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

BY WOLCOTT GIBBS, M. D.,

Rumford Professor in Harvard University.

(Continued from Vol. XVI. p. 139.)

Presented May 24th, 1881.

PHOSPHO-MOLYBDATES.

THE application of molybdic oxide to the separation and estimation of phosphoric acid has given a special interest to the phospho-molybdates, and they have accordingly been studied more or less completely by several chemists. The most thorough investigations which we possess are those of Debray,* Rammelsberg,† and Finkener,‡ but particular salts have been examined by others, and these will be noticed under the appropriate special headings.

Phospho-molybdates appear to be formed whenever phosphoric acid or a soluble phosphate is brought into solution with a molybdate, the presence of a free acid not being essential. They are also formed when phosphates and molybdates are fused together, when molybdates insoluble in water are dissolved in phosphoric acid, when molybdic oxide is digested with an alkaline phosphate, and when insoluble phosphates and molybdates are treated together with a dilute acid. As a class, they are better defined and more easy to obtain pure than the phospho-tungstates which in many respects they closely resemble. When phospho-molybdates of fixed alkaline bases are heated, they at first give off water of crystallization, and by careful heating may be obtained anhydrous. In some cases, however, molybdic oxide is volatilized even from salts containing fixed alkaline bases.

* Bull. Soc. Chim., [2.] v. 404.

† Berichte der Deutschen Chem. Gesellschaft, Zehnter Jahrgang, p. 1776.

‡ Ibid., Elfter Jahrgang, p. 1638.

I did not succeed in obtaining well-defined pyro-phospho-molybdates or pyro-phospho-tungstates, though of course the residues of the ignition of the acid salts may be regarded as such. When a phospho-molybdate is dissolved in ammonia-water and a current of sulphydric acid gas is passed into the hot solution, sulpho-molybdates are formed in large quantity. This reaction distinguishes the phospho-molybdates from the phospho-tungstates which are not decomposed under the same circumstances.

Analytical Methods.—The determination of the sum of the percentages of molybdic and phosphoric oxides was usually effected, as in the case of the phospho-tungstates, by precipitating the two oxides together by mercurous nitrate with addition of mercuric oxide to neutralize the free nitric acid. It is best to precipitate from a boiling solution, and to boil for a short time after adding mercuric oxide. This last must always be in small excess. On account of the volatility of molybdic tetroxide, it is not possible to determine directly the sum of the weights of the two oxides by simple ignition, but the difficulty may be readily overcome by the following process. The filter with the mercurous salts is to be cautiously heated in a platinum crucible properly inclined to the vertical axis of the flame until the filter is completely carbonized. On then regulating the heat and the supply of air, the carbon may be readily burned off, leaving a mass of mercurous salts mixed with more or less mercuric oxide, no weighable amount of molybdic tetroxide being lost. An accurately weighed quantity of anhydrous normal sodic tungstate in fine powder is then to be added, and the contents of the crucible carefully mixed together with a stout platinum wire previously weighed with the crucible itself. The whole is to be heated at first by radiation from a small iron dish, and afterward directly, until a clear white fused mass is obtained. A second ignition and second weighing will determine whether every trace of mercury has been expelled. It is almost needless to remark, that all these operations must be conducted under a flue with a good draught. This process gives excellent results, and is much less tedious than would perhaps be supposed.

After the estimation of the phosphoric oxide the molybdic tetroxide is best determined by difference from the sum of the weights of the two oxides found as above. No really good general method for the quantitative separation and estimation of molybdic oxide has yet been given, at least no one which is sufficiently accurate to serve as a check upon the method above described. The ammonium salts of this series are most simply analyzed by igniting them directly with sodic tung-

state, when the loss of weight corresponds to the sum of the water and ammonia.

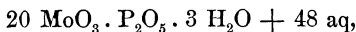
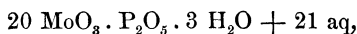
As in the case of the phospho-tungstates, the quantitative determination of phosphoric oxide is a matter of considerable difficulty. The method of separation by means of magnesia mixture has been carefully studied by Dr. Gooch, to whose paper I have already referred.* Dr. Gooch found it necessary to precipitate the ammonio-magnesian phosphate a second time, a single precipitation giving an error amounting sometimes to 6 or 7% of the phosphoric acid present. After re-solution and precipitation by ammonia, the mean error amounted to only 0.65%, which makes an almost insensible correction when the quantity of phosphoric oxide is small. In a few instances I have applied this correction after a double precipitation, but I prefer to employ the following method, which gives an almost perfect separation from molybdic tetroxide. The phosphoric oxide is first precipitated from a hot solution as ammonio-magnesian phosphate, the supernatant liquid after complete subsidence carefully decanted upon an asbestos filter, the precipitate washed with magnesia mixture and ammonia, then redissolved in the least possible quantity of hot dilute chlorhydric acid and reprecipitated with ammonia. After complete subsidence and decantation, the precipitate is boiled with successive portions of a solution of ammoniac sulphide. A more or less dark orange-red solution of ammoniac sulpho-molybdate is always obtained at first, but after two or three repetitions of the process the ammoniac sulphide added remains colorless on heating. The ammonio-magnesian phosphate is then filtered upon the asbestos filter already employed. In place of this method I have sometimes employed the following modification, which gives, I think, equally good results. After the first precipitation the phosphate is to be redissolved, and the hot solution precipitated at once by ammoniac sulphide in excess. The precipitated phosphate is then to be boiled two or three times with ammoniac sulphide as above. Whatever inaccuracy is inherent in this method depends, in my judgment, upon the fact that, as Dr. Gooch has shown, the determination of phosphoric acid by means of magnesia is, under the most favorable circumstances, a less accurate process than has been supposed.

The determination of ammonia and the alkalis was effected by the methods already described in the case of the phospho-tungstates. Water must be estimated by ignition with sodic tungstate, as there is

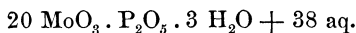
* Proceedings of American Academy, Vol. XV. p. 53.

often volatilization of molybdic teroxide when a phospho-molybdate is ignited at a temperature sufficient to expel its water. The analyses require great care and no small amount of practice to insure good results. As in the case of the phospho-tungstates, the alkaline bases are best determined by difference.

Twenty-four Atom Series. — Phospho-molybdic acid. The acid of this series was first obtained by Debray, who prepared it by boiling ammoniac phospho-molybdate with nitro-muriatic acid, and allowing the solution to evaporate spontaneously. I find that this is a good method of obtaining the acid, but the following details should be observed. The bright yellow ammoniac phospho-molybdate should be first dried, and then heated with a large excess of strong aqua-regia in a casserole over an iron capsule to serve as a radiator. In this manner the decomposition proceeds very regularly and without succussions. When it becomes necessary to add fresh acid, the supernatant liquid should be allowed to settle completely and then be poured off carefully. Fresh acid may then be added, and the process, which is at best a slow one, continued. When the ammonium salt has disappeared, the liquid is to be evaporated until the excess of nitric and chlorhydric acids has been expelled. On standing, large bright yellow octahedral crystals are obtained from the very concentrated solution. These may be redissolved and recrystallized, but there is always some loss in the process of purification, because solution in water produces more or less decomposition of the acid with formation of a pale greenish white crystalline body. This substance passes very readily through a filter, and the solution of the acid must be allowed to settle completely before the clear supernatant liquid is brought upon the filter. Debray obtained three different hydrates of phospho-molybdic acid, to which he gave, respectively, the formulas



and

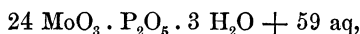


Unfortunately he has not given either the methods or the complete results of his analyses. In the first hydrate he found 13.30%, in the second 23.40%, and in the the third 19.60% of water.

I obtained the acid only in transparent octahedral crystals which had a bright yellow color. Of these crystals, dried by pressure with woollen paper,

0.9945 gr. lost by ignition with WO_4Na_2 0.2362 gr. = 23.75% water.
 1.4588 gr. gave 0.0713 gr. $\text{P}_2\text{O}_7\text{Mg}_2$ = 3.12% P_2O_5 .

The analysis leads to the formula



which requires:—

		Calc'd.	Found.
24 MoO_3	3456	73.31	73.13
P_2O_5	142	3.01	3.12
62 H_2O	1116	23.68	23.75
	4714	100.00	

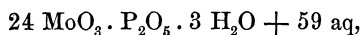
The phosphoric oxide was determined by double precipitation and treatment with ammoniac sulphide. The molybdic oxide was estimated by difference. The crystallized acid effloresces so readily that the precise determination of the water is difficult. In a portion of the crystals which had effloresced in a very marked degree, —

0.9873 gr. lost on ignition with WO_4Na_2 0.1760 gr. = 17.82% water
 2.2472 gr. gave 0.1163 gr. $\text{P}_2\text{O}_7\text{Mg}_2$ = 3.31% P_2O_5

The ratio of the molybdic to the phosphoric oxide is in this analysis also 24 : 1 ; and, if we compute the results of both analyses for an anhydrous compound of the two oxides, we find:—

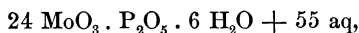
		Calc'd.		
24 MoO_3	3456	96.06	95.91	95.97
P_2O_5	142	3.94	4.09	4.03
	3598	100.00	100.00	100.00

The analyses leave, I think, no reasonable doubt as to the ratio of the two oxides. Phospho-molybdic acid therefore corresponds in composition with phospho-tungstic acid, the ratio of the two oxides being 24:1, as given by Finkener,* and not 20:1, as stated by Debray. With respect, however, to the number of atoms of water in the crystallized octahedral hydrate, I may remark that, while the analysis agrees best with the formula given,

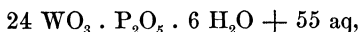


* *Loc. cit.*

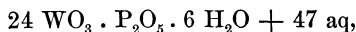
it is much more probable that the acid really contains an atom less of water, and that its formula, apart from the question of basicity, is



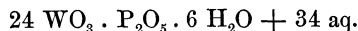
like



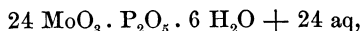
already described. This formula requires 23.38% water, instead of 23.75%, as found. Debray found 23.40%. As already stated, the crystals analyzed were dried by pressure with woollen paper, after draining off a syrupy mother liquor, and may therefore not have been perfectly free from extraneous water. Finally, the analyses of Finkener led also to the formula with 61 atoms of water, and I shall adopt this as the definite constitution of the octahedral hydrate. Finkener's work has not yet been published in detail; but from the abstract which he has given, it clearly appears that we owe to him the establishment of the true constitution of the only phospho-molybdic acid yet obtained. As already mentioned, there are two other hydrates of phospho-tungstic acid, having, respectively, the formulas



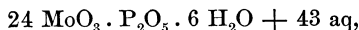
and



The two hydrates of phospho-molybdic acid described by Debray would correspond to the formulas



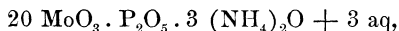
and



if we suppose them, as is most probable, to belong to the 24-atom series. The first formula requires 13.05%, the second 19.66% water; Debray found 13.09 % and 19.60 %. Finkener obtained still another hydrate, containing about 32 atoms of water, basic water included.

Phospho-molybdic acid dissolves very readily in water, forming a colorless liquid which has a strong acid reaction. As already stated, the solution is always accompanied by a slight decomposition, with formation of a very pale greenish white crystalline substance. A precisely similar decomposition is observed in the solution of the corresponding phospho-tungstic acid. The crystals lose all their water when slightly ignited. According to Finkener, three atoms of water remain at 140° C. The solution readily expels carbonic dioxide from the alkaline carbonates. The question of the basicity of the acid will be discussed farther on.

24 : 3 *Ammonic Phospho-molybdate*. — The constitution of the beautiful yellow salt which is formed when an excess of a mineral acid is added to a solution containing molybdic and phosphoric oxides and a salt of ammonium, has long been in dispute. The analyses of Svanberg and Struve,* Nutzinger,† Sonnenschein,‡ Lipowitz,§ and Seligsohn,|| gave results which differed very sensibly from each other, according to the method of analysis employed. Debray gave the formula



but without the details of his analysis. More recently the subject has been examined with great care by Finkener,¶ who has arrived at the conclusion that, though the percentages of water and ammonia may vary within wide limits, the ratio of the molybdic and phosphoric oxides is always as 24 : 1.

With respect to the preparation and properties of the yellow ammonium salt, I have little to add to what has been done by these chemists. I repeatedly prepared the salt for analysis, usually by mixing solutions of ammonic molybdate — 7 : 3 salt — and phosphate, adding nitric acid in excess to the solution, and boiling. When the mixed solution is boiled for a short time, the precipitation of the yellow salt is complete after standing until the liquid becomes cold. In the publication of this result, which is important in analysis, I have been anticipated by Atterberg; ** but I propose in another paper to give the results of my work on the quantitative determination of phosphoric acid, and will then give ample details.

As regards the composition of the yellow phospho-molybdates of ammonium, my results do not agree with those of Finkener, as I think I have evidence that, as in the case of the phospho-tungstates, there are series of phospho-molybdates in which the ratio of the molybdic to the phosphoric oxide is as 20 : 1, as 22 : 1, and as 24 : 1. In one preparation, —

1.1492 gr. lost on ignition with WO_4Na_2 0.0827 gr. NH_3 and H_2O
 $= 7.20\%$

* Journal für prakt. Chemie, xlv. 291.

† Pharmaceut. Vierteljahresschrift, iv. 549.

‡ Journal für prakt. Chemie, liii. 342.

§ Poggendorff's Annalen, cix. 135.

|| Journal für prakt. Chemie, lxvii. 470.

¶ *Loc cit.*

** Berichte der Chem. Gesellschaft, 1881, p. 1217.

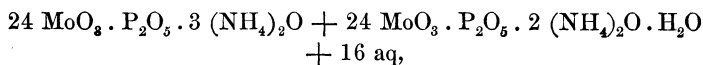
0.5905 gr. lost on ignition with WO_4Na_2 0.0432 gr. NH_3 and H_2O
 $= 7.31\%$

1.7158 gr. gave 0.1027 gr. $\text{P}_2\text{O}_7\text{Mg}_2 = 3.83\% \text{P}_2\text{O}_5$

0.9806 gr. " 0.0567 gr. $\text{P}_2\text{O}_7\text{Mg}_2 = 3.70\% \text{P}_2\text{O}_5$

1.8903 gr. " 0.1321 gr. $\text{NH}_4\text{Cl} = 3.20\% (\text{NH}_4)_2\text{O}$

In these analyses, the first determination of the phosphoric oxide was made by double precipitation only, without subsequent treatment with ammoniac sulphide; but in the second, this reagent was employed in the manner above described. The ratio of MoO_3 to P_2O_5 is almost precisely 24:1, and the analyses correspond closely with the formula

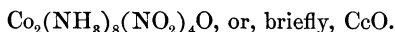


which requires:—

		Calc'd.	Mean.		
48 MoO_3	6912	89.05	89.00	—	—
2 P_2O_5	284	3.66	3.75	3.70	3.83
5 $(\text{NH}_4)_2\text{O}$	260	3.35	3.39		3.39
17 H_2O	306	3.94	3.86	3.81	3.92
	7762	100.00	100.00		

Acid salts of similar type occur frequently in the class of phosphomolybdates, as in that of phospho-tungstates.

24:1 *Croceo-cobalt Salt*. — The disposition of the cobaltamines to form highly crystalline compounds, together with their well-defined and various degrees of basicity, led me to study the relations of these bases to the phospho-molybdic acids. This had already been done to a certain extent with the 5:1 atom series by Jörgensen, whose results I shall cite in connection with that series. Neither roseo-cobalt nor luteo-cobalt forms well-defined salts with 24:1 phospho-molybdic acid. I had therefore recourse to croceo-cobalt,* the oxide of which may be written



The chloride of this series gives no precipitate with solutions of 7:3 ammoniac molybdate, or of hydro-disodic phosphate; but in an acid solution of these two salts a solution of the chloride throws down a beautiful bright yellow highly crystalline salt, which may be washed with cold water. The portion analyzed was dried on woollen paper only. Of this salt, —

* Proceedings of American Academy, Vol. X. p. 1.

$$\begin{array}{lcl} 1.0728 \text{ gr. gave } 0.8133 \text{ gr. MoO}_3 + \text{P}_2\text{O}_5 = 75.81\% \\ 1.4520 \text{ gr. " } 0.4719 \text{ gr. P}_2\text{O}_5 = 2.96\% \end{array}$$

This corresponds to 72.85% MoO₃ by difference, and 24.19% of CcO and water by the loss. The analyses agree very closely with the formula



which requires:—

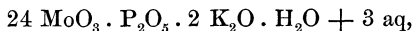
		Calc'd.	
24 MoO ₃	3456	72.82	72.86
P ₂ O ₅	142	2.99	2.96
CcO	734	15.47	} 24.19 { 24.19
23 H ₂ O	414	8.72	
	4746	100.00	

Under the microscope this salt is seen to consist of fine yellow felted needles. It is very slightly soluble in cold water, but is soluble in a rather large quantity of boiling water, giving an orange-yellow solution, with a strongly acid reaction. The solution gives with argentic nitrate a very insoluble sulphur-yellow flocky precipitate, which after a time becomes crystalline, and a pale yellow flocky precipitate with mercurous nitrate. No precipitate is formed with cupric sulphate or baric chloride. The salt could not be recrystallized; it is interesting as a particularly well-defined soluble acid salt of the 24:1 atom series.

24:2 Acid Potassium Salt.—This salt was prepared by boiling together solutions of potassic molybdate and phosphate, adding an excess of nitric acid, and boiling the whole for some time. As in the case of the ammonium salts, the precipitation is greatly facilitated by this process, taking place very slowly in the cold. The salt obtained was in very minute crystals, bright yellow, and but slightly soluble in cold water. Of this salt,—

$$\begin{array}{lcl} 0.7772 \text{ gr. lost on ignition } 0.0128 \text{ gr.} & = & 1.64\% \text{ water} \\ 0.7962 \text{ gr. " " } 0.0130 \text{ gr.} & = & 1.66\% \text{ " } \\ 1.1703 \text{ gr. gave } 1.0895 \text{ gr. MoO}_3 + \text{P}_2\text{O}_5 = 93.10\% \\ 1.3263 \text{ gr. " } 0.0779 \text{ gr. P}_2\text{O}_7\text{Mg}_2 & = & 3.76\% \text{ P}_2\text{O}_5 \\ 1.3033 \text{ gr. " } 0.0778 \text{ gr. " } & = & 3.82\% \text{ " } \end{array}$$

The phosphoric oxide was twice precipitated as ammonio-magnesian phosphate. The analyses correspond with the formula

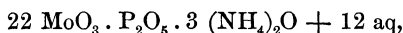


which requires:—

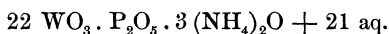
		Calc'd.		
24 MoO ₃	3456	89.55	89.31	
P ₂ O ₅	142	3.69	3.76	3.82
2 K ₂ O	189	4.90		5.25
4 H ₂ O	72	1.86	1.66	1.64
	3859	100.00		

Twenty-two Atom Series.— In the paper already referred to, Ram-
melsberg has described several salts in which he found the ratio of
molybdic to phosphoric oxide as 22 : 1. Unfortunately, he has not
given the method of analysis which he employed, and in a question of
so much difficulty and delicacy it is, to say the least, extremely desira-
ble to know what degree of precision may be expected in the analyses.
As his results appear to be supported by my own, I shall adopt them,
leaving to the further progress of analytical chemistry the final settle-
ment of the few doubtful points.

22 : 3 *Ammonium Salt.*— Rammelsberg found for the neutral salt
of this series the formula



which corresponds, except as regards the amount of water of crystalli-
zation, with a phospho-tungstate which I have already described, —



In one preparation of a yellow insoluble ammonium salt exactly
resembling the corresponding salt of the 24-atom series, —

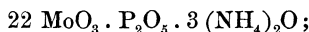
1.6885 gr., lost on ignition with WO_4Na_2 0.0873 gr. = 5.17% NH_3
and H_2O

1.7764 gr. gave 0.6200 gr. $\text{P}_2\text{O}_7\text{Mg}_2$ = 4.17% P_2O_5 .

1.9024 gr. “ 0.6029 gr. “ = 4.01% “

1.2334 gr. “ 0.6262 gr. NH_4Cl = 4.23% $(\text{NH}_4)_2\text{O}$.

The salt was dried for some time *in pleno* over sulphuric acid, and
had evidently lost water of crystallization. If we deduct the remain-
ing water, 0.94%, and calculate the analysis for an anhydrous salt,
we have for the formula



		Calc'd.	
22 MoO ₃	3168	91.41	91.68
P ₂ O ₅	142	4.09	4.05
3 (NH ₄) ₂ O	156	4.50	4.27
	3466	100.00	

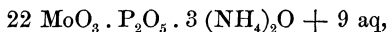
In another preparation, —

1.0324 gr. lost on ignition with WO_4Na_2 0.0922 gr. = 8.33% NH_3
and H_2O

2.0670 gr. gave 0.1255 gr. P_2O_5 Mg_2 = 3.88% P_2O_5

2.0352 gr. “ 0.1220 gr. “ = 3.84% “

These analyses lead to the formula



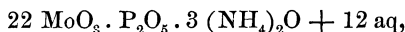
which requires: —

		Calc'd.		
22 MoO_3	3168	87.32	87.21	
P_2O_5	142	3.91	3.88	3.84
3 $(\text{NH}_4)_2\text{O}$	156	4.29	} 8.77	8.93
9 H_2O	162	4.48		
	<u>3628</u>	<u>100.00</u>		

If from the analyses of the two salts above described we calculate the composition of the combination of molybdic and phosphoric oxides supposed to be isolated, and compare this with the percentages calculated upon the two hypotheses of a ratio of 22:1 and a ratio of 24:1, we have: —

		Calc'd.	I.	II.	Calc'd.		
22 MoO_3	3168	95.76	95.76	95.76	96.06	3456	24 MoO_3
P_2O_5	142	4.24	4.24	4.24	3.94	142	P_2O_5
	<u>3310</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>3598</u>	

In both cases the phosphoric oxide was precipitated twice, but the ammonia-magnesian phosphate was not treated with ammoniac sulphide. According to the results of Dr. Gooch already cited, the probable error of this method does not exceed 1% in excess of the quantity of phosphoric oxide present. It appears, therefore, that the correction to be applied to the phosphoric oxide in the above analyses does not, at most, exceed 0.04%. The mean of Dr. Gooch's analyses would require a deduction of 0.02% only. The yellow ammonium salt analyzed by Rammelsberg corresponds to the formula



which requires (Rammelsberg): —

		Calc'd.	
22 MoO_3	3168	86.04	86.45
P_2O_5	142	3.86	3.90
3 $(\text{NH}_4)_2\text{O}$	156	4.24	3.25
12 H_2O	216	5.86	5.77
	<u>3682</u>	<u>100.00</u>	<u>99.37</u>

Rammelsberg gives these figures as the means of several analyses which agree well with each other, but it must be admitted that a closer correspondence with the percentages required by the formulas would have been desirable. The comparison is not given in his paper. The air-dried salt loses all its water over sulphuric acid. The three atoms of basic water, if we assume their existence, must therefore be united by a very feeble affinity. Rammelsberg has also analyzed the corresponding potassic salt of the same series. I here give his results, for the sake of comparison with the formula:—

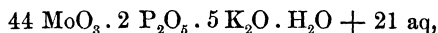
		Calc'd.	
22 MoO ₃	3168	83.17	84.43
P ₂ O ₅	142	3.73	3.78
3 K ₂ O	283	7.43	6.86
12 H ₂ O	216	5.67	5.55
	3809	100.00	100.62

This salt loses all its water between 120° and 140°. In judging the results of these analyses, as well as of those which I have given, it must be carefully borne in mind that the salts themselves cannot be recrystallized, and that consequently their absolute purity cannot be guaranteed. Moreover, if—as I believe I have shown—there are very similar salts which represent three series in which the ratios of the molybdic and phosphoric oxides are respectively as 24:1, 22:1, and 20:1, we may, at least occasionally, have mixtures of the salts of three, or of any two series. The difficulty here is precisely that which occurs in the case of the phospho-tungstates.

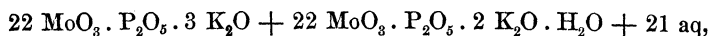
44:2 *Acid Potassium Salt*.—This salt was prepared by boiling a mixture of potassic molybdate and phosphate with nitric acid in excess, when a beautiful yellow crystalline powder separated. This was washed with cold water and dried on woollen paper. Of this salt, —

0.9850 gr. lost on ignition 0.0521 gr. = 5.28% water.
 0.8983 gr. gave 0.7943 gr. MoO₃ + P₂O₅ = 88.42%
 2.0617 gr. gave 0.1201 gr. P₂O₇Mg₂ = 3.72%

These analyses lead to the formula



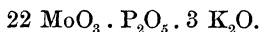
or



which requires:—

		Calc'd.	
44 MoO ₃	6336	84.62	84.70
2 P ₂ O ₅	284	3.79	3.72
5 K ₂ O	472	6.30	6.30 (diff.)
22 H ₂ O	396	5.29	5.28
	<u>7488</u>	<u>100.00</u>	

The salt is therefore the acid salt corresponding to a neutral salt with the formula



Rammelsberg's analyses agree better with the formula of the acid salt given above than with that of the neutral compound assumed by him.

Twenty Atom Series.—The only salt of this series which I have obtained is one of ammonium prepared like the salts already described, having like these a fine yellow color and a very fine-grained crystalline structure, and like them but slightly soluble in water. Of this salt,—

1.0936 gr. lost on ignition with WO₄Na₂ 0.0729 gr. = 6.66% NH₃
and H₂O

1.8183 gr. lost on ignition with WO₄Na₂ 0.1155 gr. = 6.35% NH₃
and H₂O

0.8862 gr. gave 0.6153 gr. NH₄Cl = 4.12% (NH₄)₂O

1.3213 gr. gave 0.6224 gr. P₂O₇Mg₂ = 4.19% P₂O₅

1.5135 gr. gave 0.6349 gr. P₂O₇Mg₂ = 4.31% P₂O₅

The salt was dried on a water-bath, and afterward over sulphuric acid. The phosphoric oxide was precipitated twice, but not treated with ammoniac sulphide. The analyses lead to the formula



which requires:—

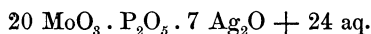
		Calc'd.			
60 MoO ₃	8640	89.09	} 93.48	89.21	} 93.52
3 P ₂ O ₅	426	4.39		4.31 4.19	
8 (NH ₄) ₂ O	416	4.29	} 6.52	4.12	} 6.50
12 H ₂ O	216	2.23		2.54	
	<u>9698</u>	<u>100.00</u>			

If we calculate the composition of the mixed oxides of molybdenum and phosphorus existing in this salt we have:—

		Calc'd.	
20 MoO ₃	2880	95.30	95.39
P ₂ O ₅	142	4.70	4.61
	<u>3022</u>	<u>100.00</u>	<u>100.00</u>

It will be seen that the ratio is here very nearly as 20 : 1. This may however be merely accidental, and farther researches are necessary to fully establish the existence of a 20-atom series.

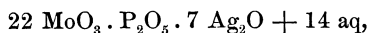
According to Debray a solution of argentic nitrate gives with one of phospho-molybdic acid a precipitate which soon becomes crystalline, and which has the formula



Such a salt would possess a twofold interest, first, as another evidence of the existence of a 20-atom series of phospho-molybdates, and, secondly, as showing that the acid of the series may unite with more than *six* atoms of base. On mixing the two solutions as above, I obtained a precipitate in small indistinct crystals of a greenish yellow color. These crystals were soluble in hot water, but the solution was quickly decomposed with precipitation of a white powder. Under the microscope with a high power and transmitted light the salt appeared to consist of small tabular crystals mixed with a few long yellow prisms of very different habitus. Of this compound, —

1.3604 gr. lost by ignition with WO₄Na₂ 0.0692 gr. water = 5.08%
 2.1099 gr. gave 0.8287 gr. AgCl = 31.63% Ag₂O
 0.6733 gr. gave 0.2619 gr. AgCl = 31.44% Ag₂O
 2.1099 gr. gave 0.0928 gr. P₂O₅Mg₂ = 2.81% P₂O₅

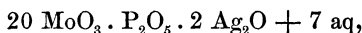
The phosphoric oxide was determined in the filtrate from the argentic chloride by double precipitation and treatment with ammoniac sulphide. The ratio of the molybdic to the phosphoric oxide is as 21 : 1, but the formula which most nearly represents the analysis is



which requires, —

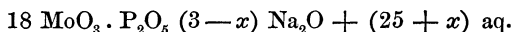
		Calc'd.		
22 MoO ₃	3168	61.08	60.57	
P ₂ O ₅	142	2.74	2.81	
7 Ag ₂ O	1624	31.32	31.44	31.63
14 H ₂ O	<u>252</u>	<u>4.86</u>		<u>5.08</u>
	5186	100.00		

The only conclusion which can fairly be drawn from the analysis is that there is at least one phospho-molybdate in which the number of atoms of base exceeds three. It is certain that the salt does not represent a perfectly definite and homogeneous compound, and it may possibly be a mixture of the 20-atom salt, $20 \text{ MoO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{ Ag}_2\text{O}$, and an acid molybdate of silver, $2 \text{ MoO}_3 \cdot \text{Ag}_2\text{O}$, nearly in atomic proportions. By dissolving the salt in nitric acid and evaporating, Debray obtained another salt in small brilliant yellow crystals. For this salt he proposes the formula



but as usual he has given no analyses.

Eighteen Atom Series. — I have myself met with no salts belonging to this series, but according to Finkener* there are sodium salts corresponding to the general formula



These salts are yellow and easily soluble.

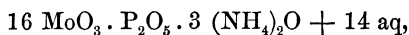
Sixteen Atom Series. — *16 : 3 Ammonium Salt.* — In preparing the 5 : 3 atom ammonium salt a white crystalline precipitate was formed, insoluble in cold, but soluble with decomposition in much boiling water, and easily soluble in ammonia. In this salt dried over sulphuric acid, —

0.5100 gr. lost by ignition with WO_4Na_2 0.0722 gr. = 14.16% NH_3
and H_2O

1.1653 gr. gave 0.1259 gr. NH_4Cl = 5.25% $(\text{NH}_4)_2\text{O}$

0.8114 gr. gave 0.0658 gr. $\text{P}_2\text{O}_7\text{Mg}_2$ = 5.19% P_2O_5

The analysis corresponds with the formula

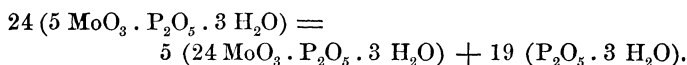


which requires, —

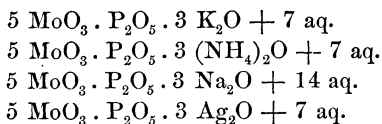
		Calc'd.	Found.
16 MoO_3	2304	80.73	80.65
P_2O_5	142	4.97	5.19
3 $(\text{NH}_4)_2\text{O}$	156	5.46	5.25
14 H_2O	252	8.84	8.91
	<hr/> 2854	<hr/> 100.00	

* *Loc. cit.*, p. 1639.

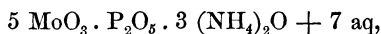
Five to One Series.—Salts of this series were discovered at an early period in the history of the subject by Zenker.* The ammonium salt was analyzed by Zenker† and Werncke,‡ and recently by Rammelsberg.§ Debray obtained the same salt, but has published no analyses. Rammelsberg also obtained the corresponding potassium salt, as well as an acid salt of the same series. The alkaline salts are colorless, and separate in well-defined crystals, which are usually easily soluble in water. The acid of the series, as Debray has stated, cannot be obtained by the decomposition of its salts, being resolved by acids into free phosphoric acid and salts of the 24-atom series. The decomposition may probably be expressed by the equation



All the neutral salts are tribasic (old style) or more correctly hexatomic, but well-defined acid salts exist in which the ratio of the molybdic oxide to the fixed base is as 10 : 5. Such salts have been obtained by Rammelsberg and by myself. The salts of the higher series are decomposed by alkalis, as stated by Debray, salts of the 5-atom series and alkaline molybdates being formed. Conversely, when a mineral acid is added to a solution of an alkaline salt of the 5-atom series, a salt of a higher series is formed, frequently as a yellow crystalline precipitate. The neutral salts of this series hitherto described have respectively the formulas



5 : 3 Phospho-molybdate of Ammonium.—This beautiful salt appears, as already stated, to have been first obtained by Zenker. It is readily obtained by dissolving together five molecules of ammonic molybdate and two of ammonic phosphate, and evaporating the solution, when beautiful prismatic crystals, with a glassy lustre, separate. These may easily be purified by recrystallization. The salt is readily soluble in hot, less easily in cold water. The solution has an acid reaction. Zenker's analyses, as well as those of Werncke, agree closely with the formula



* Journal für prakt. Chemie, lviii. 256.

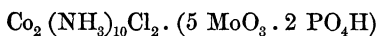
† Loc. cit.

‡ Zeitschrift für Analyt. Chemie, xiv. 12.

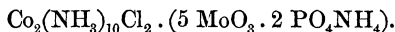
§ Loc. cit.

in which formula the phospho-molybdic acid is regarded as tribasic. Debray gives the same formula, without details of analysis, and Rammelsberg has very recently again analyzed the salt, confirming the results of Zenker. The salt in question is particularly interesting, first, because the number of atoms of molybdic oxide is *uneven*; and secondly, because the basicity of the acid appears to be 3, and not 6, even when the salt has separated from neutral solutions.

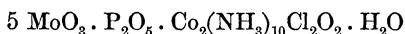
Jørgensen * has described two well-defined crystalline salts belonging to this series and having according to his notation respectively the formulas



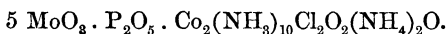
and



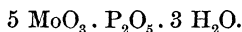
I should write these



and



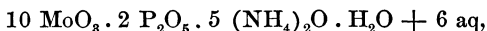
It will readily be seen that both salts correspond to the acid represented by the formula



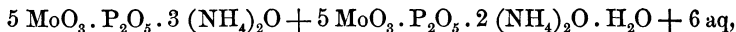
Acid 10 : 5 Ammonium Salt. — When ammonic phosphate is dissolved in boiling water, and molybdic oxide is added in small portions at a time, the oxide readily dissolves, but a greater or less quantity of a white insoluble crystalline salt is formed. The filtrate deposits on evaporation large colorless crystals, which appear to be either trimetric or monoclinic. Of these crystals, —

1.1126 gr. lost on ignition with WO_4Na_2	0.2076 gr. = 18.66% NH_3 and H_2O .
1.2962 gr. “ “ “	0.2425 gr. = 18.71% “
1.2165 gr. “ “ “	0.2247 gr. = 18.47% “
0.9263 gr. gave 0.1912 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 13.20% P_2O_5
1.0540 gr. “ 0.2196 gr. “	= 13.32% “
1.1824 gr. “ 0.3018 gr. NH_4Cl	= 12.41% $(\text{NH}_4)_2\text{O}$
1.0183 gr. “ 0.2563 gr. “	= 12.23% “
1.6430 gr. “ 0.4168 gr. “	= 12.32% “

The analyses lead to the formula



or



which requires:—

		Calc'd.	Mean.			
10 MoO ₃	1440	68.24	68.13
2 P ₂ O ₅	284	13.46	13.26	13.20	13.32	...
5 (NH ₄) ₂ O	260	12.32	12.32	12.41	12.23	12.32
7 H ₂ O	126	5.98	6.29	6.15	6.34	6.39
	2110	100.00				

The phosphoric oxide was determined by double precipitation only, without subsequent treatment with ammoniac sulphide. The percentage is a little lower than that required by the formula, which is unusual; but the general agreement of the analyses with the formula is satisfactory. Rammelsberg has described an acid potassium salt with the formula



It is therefore at least probable that we shall find another ammonia salt with 20 atoms of water, and another potassium salt with 7 atoms. Zenker has described another potassic salt to which he gives the formula,—as I should write it,—



but the results of his analyses differ very widely from the percentages required by the formula, and on repeating his process I obtained only the 10 : 5 atom salt of Rammelsberg. The formula given above for this salt requires 11.11% P₂O₅. I found 11.22%.

Rammelsberg* has also described a white insoluble potassium salt to which he gives the formula 15 MoO₃ · P₂O₅ · 5 K₂O, but without any statement of his analyses.

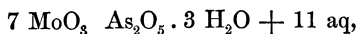
ARSENIO-MOLYBDATES.

Compounds of arsenic and molybdic oxides have been described by Seyberth† and by Debray.‡ Seyberth obtained an acid with the formula,—as I should write it,—

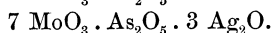
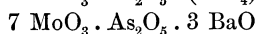
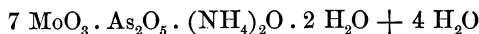
* *Loc. cit.*

† Berichte der Chem. Gesellschaft, 1874, p. 391.

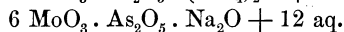
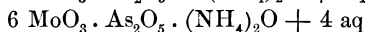
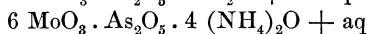
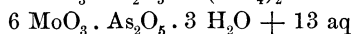
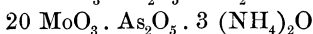
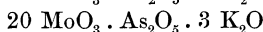
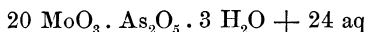
‡ Comptes Rendus, lxxviii. 1408.



and the three corresponding salts : —



Debray obtained the acids and one or two salts of two different series, which may be represented respectively by the formulas : —



Debray considers the formula of the 20-atom ammonium salt as probable only, and regards the water determination in the corresponding acid as not quite certain. Neither Seyberth nor Debray has described the analytical methods employed, or given the details of the analyses.

I have found it most advantageous to separate arsenic from molybdc oxide by precipitating with magnesia mixture, redissolving the ammonio-magnesian arsenate, and precipitating a second time with ammonia after adding a little magnesia mixture. The ammonio-magnesian arsenate may be digested with ammoniac sulphide without decomposition; but after the second precipitation it does not retain molybdc oxide, and the subsequent treatment is therefore unnecessary. To determine the sum of the molybdc and arsenic oxides I precipitate the two together with mercurous nitrate and mercuric oxide, in the manner already described for the estimation of molybdc and phosphoric oxides, filter upon paper, and after drying roll up the filter and its contents and ignite cautiously in a porcelain crucible. By slow and careful heating the filter may be completely burned without loss of molybdc or arsenic oxides, this result being attained by the oxygen of the mercurous and mercuric oxides present. A weighed quantity of sodic tungstate is then to be added in fine powder, the mass well mixed in the crucible, and then cautiously heated until mercury is completely expelled, and after cooling a white fused mass remains. A second or even a third heating is necessary to insure a

perfectly constant weight. The difference between the percentage of arsenic oxide, As_2O_5 , and the sum of the percentages of the arsenic and molybdic oxides, gives the percentage of molybdic oxide with a very fair degree of approximation. In these salts the water must always be determined by ignition with sodic tungstate or some similar compound, since both arsenic and molybdic oxides are volatile.

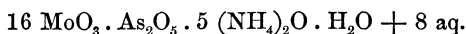
Sixteen to one Series.—When solutions of ammoniac arsenate and acid molybdate (7 : 3 salt) are mixed, a beautiful white crystalline precipitate is thrown down, which is very insoluble in cold water but dissolves slightly in boiling water, giving, however, a turbid solution. The salt is readily soluble in ammonia water. The portion analyzed was well washed on a filter with cold water and dried on woollen paper. In this salt, —

1.1322 gr. lost on ignition with WO_4Na_2 0.1636 gr. NH_3 and H_2O
 = 14.45%

1.3389 gr. gave 0.2481 gr. NH_4Cl = 9.00% $(\text{NH}_4)_2\text{O}$

1.4276 gr. “ 0.1478 gr. $\text{As}_2\text{O}_7\text{Mg}_2$ = 7.68% As_2O_5

The analyses lead to the formula



which requires : —

		Calc'd.		
16 MoO_3	2304	77.94	} 85.72	77.97
As_2O_5	230	7.78		7.68
5 $(\text{NH}_4)_2\text{O}$	260	8.79	} 14.28	9.00
9 H_2O	162	5.49		5.45
	<hr/> 2956			

The salt may have lost a little ammonia in drying. When potassic arsenate and acid molybdate are mixed, a similar salt is formed. A solution of arsenic acid gives at once in solutions of acid ammoniac or potassic molybdate a beautiful white crystalline precipitate, insoluble in cold water, but soluble in a large quantity of boiling water, forming cloudy solutions which pass freely through a filter. These may serve as starting-points for new investigations. The arsenio-molybdate above described is not perceptibly altered by long boiling with nitric acid, but the existence of higher compounds containing 22 or 24 molecules of molybdic to one of arsenic oxide appears at least extremely probable.

The phospho-molybdates and arsenio-molybdates now known with some degree of certainty are as follows : —

24 MoO ₃ . P ₂ O ₅ . 6 H ₂ O + 47 aq	Mo ₂₄ P ₂ O ₇₁ (HO) ₁₂ + 47 aq
24 MoO ₃ . P ₂ O ₅ . 6 H ₂ O + 43 aq	Mo ₂₄ P ₂ O ₇₁ (HO) ₁₂ + 43 aq
24 MoO ₃ . P ₂ O ₅ . 6 H ₂ O + 24 aq	Mo ₂₄ P ₂ O ₇₁ (HO) ₁₂ + 24 aq
24 MoO ₃ . P ₂ O ₅ . 2 K ₂ O . 4 H ₂ O	Mo ₂₄ P ₂ O ₇₁ (KO) ₄ (HO) ₈
24 MoO ₃ . P ₂ O ₅ . CcO . 5 H ₂ O + 18 aq	Mo ₂₄ P ₂ O ₇₁ (CcO ₂)(HO) ₁₀ + 18 aq
48 MoO ₃ . 2 P ₂ O ₅ . 5 (NH ₄) ₂ O . H ₂ O + 16 aq	Mo ₄₈ P ₄ O ₁₄₈ (NH ₄ O) ₁₀ (HO) ₂ + 16 aq
22 MoO ₃ . P ₂ O ₅ . 3 (NH ₄) ₂ O . 3 H ₂ O + 9 aq	Mo ₂₂ P ₂ O ₆₅ (NH ₄ O) ₆ (HO) ₆ + 9 aq
22 MoO ₃ . P ₂ O ₅ . 3 (NH ₄) ₂ O . 3 H ₂ O + 6 aq	Mo ₂₂ P ₂ O ₆₅ (NH ₄ O) ₆ (HO) ₆ + 6 aq
22 MoO ₃ . P ₂ O ₅ . 3 (NH ₄) ₂ O	Mo ₂₂ P ₂ O ₆₅ (NH ₄ O) ₆
22 MoO ₃ . P ₂ O ₅ . 3 K ₂ O . 3 H ₂ O + 9 aq	Mo ₂₂ P ₂ O ₆₅ (KO) ₆ (HO) ₆ + 9 aq
22 MoO ₃ . P ₂ O ₅ . 7 Ag ₂ O + 14 aq	Mo ₂₂ P ₂ O ₆₄ (AgO) ₁₄ + 14 aq
44 MoO ₃ . 2 P ₂ O ₅ . 5 K ₂ O . H ₂ O + 21 aq	Mo ₄₄ P ₄ O ₁₃₆ (KO) ₁₀ (HO) ₂ + 21 aq
60 MoO ₃ . 3 P ₂ O ₅ . 8 (NH ₄) ₂ O . H ₂ O + 11 aq	Mo ₆₀ P ₆ O ₁₈₆ (NH ₄ O) ₁₆ (HO) ₂ + 11 aq
18 MoO ₃ . P ₂ O ₅ . Na ₂ O . 5 H ₂ O + m aq	Mo ₁₈ P ₂ O ₅₈ (NaO) ₂ (HO) ₁₀ + m aq
18 MoO ₃ . P ₂ O ₅ . 2 Na ₂ O . 4 H ₂ O + n aq	Mo ₁₈ P ₂ O ₅₈ (NaO) ₄ (HO) ₈ + n aq
16 MoO ₃ . P ₂ O ₅ . 3 (NH ₄) ₂ O . 3 H ₂ O + 11 aq	Mo ₁₆ P ₂ O ₄₇ (NH ₄ O) ₆ (HO) ₆ + 11 aq
5 MoO ₃ . P ₂ O ₅ . 3 Na ₂ O . 3 H ₂ O + 11 aq	Mo ₅ P ₂ O ₁₄ (NaO) ₆ (HO) ₆ + 11 aq
5 MoO ₃ . P ₂ O ₅ . 3 (NH ₄) ₂ O . 3 H ₂ O + 4 aq	Mo ₅ P ₂ O ₁₄ (NH ₄ O) ₆ (HO) ₆ + 4 aq
5 MoO ₃ . P ₂ O ₅ . 3 K ₂ O . 3 H ₂ O + 4 aq	Mo ₅ P ₂ O ₁₄ (KO) ₆ (HO) ₆ + 4 aq
5 MoO ₃ . P ₂ O ₅ . 3 Ag ₂ O . 3 H ₂ O + 4 aq	Mo ₅ P ₂ O ₁₄ (AgO) ₆ (HO) ₆ + 4 aq
10 MoO ₃ . 2 P ₂ O ₅ . 5 K ₂ O . H ₂ O + 19 aq	Mo ₁₀ P ₄ O ₈₄ (KO) ₁₀ (HO) ₂ + 19 aq
10 MoO ₃ . 2 P ₂ O ₅ . 5 (NH ₄) ₂ O . H ₂ O + 6 aq	Mo ₁₀ P ₄ O ₈₄ (NH ₄ O) ₁₀ (HO) ₂ + 6 aq
20 MoO ₃ . As ₂ O ₅ . 6 H ₂ O + 21 aq	Mo ₂₀ As ₂ O ₅₉ (HO) ₁₂ + 21 aq
20 MoO ₃ . As ₂ O ₅ . 3 K ₂ O	Mo ₂₀ As ₂ O ₆₂ (KO) ₆
20 MoO ₃ . As ₂ O ₅ . 3 (NH ₄) ₂ O	Mo ₂₀ As ₂ O ₆₂ (NH ₄ O) ₆
16 MoO ₃ . As ₂ O ₅ . 5 (NH ₄) ₂ O . H ₂ O + 8 aq	Mo ₁₆ As ₂ O ₄₇ (NH ₄ O) ₁₀ (HO) ₂ + 8 aq
7 MoO ₃ . As ₂ O ₅ . 6 H ₂ O + 8 aq	Mo ₇ As ₂ O ₂₀ (HO) ₁₂ + 8 aq
7 MoO ₃ . As ₂ O ₅ . (NH ₄) ₂ O . 5 H ₂ O	Mo ₇ As ₂ O ₂₀ (NH ₄ O) ₂ (HO) ₁₀
7 MoO ₃ . As ₂ O ₅ . 3 BaO	Mo ₇ As ₂ O ₂₈ (BaO) ₃
7 MoO ₃ . As ₂ O ₅ . 3 Ag ₂ O	Mo ₇ As ₂ O ₂₈ (AgO) ₆
6 MoO ₃ . As ₂ O ₅ . 6 H ₂ O + 10 aq	Mo ₆ As ₂ O ₁₇ (HO) ₁₂ + 10 aq
6 MoO ₃ . As ₂ O ₅ . 4 (NH ₄) ₂ O + aq	Mo ₆ As ₂ O ₁₉ (NH ₄ O) ₃
6 MoO ₃ . As ₂ O ₅ . (NH ₄) ₂ O . 2 H ₂ O + 2 aq	Mo ₆ As ₂ O ₂₀ (NH ₄ O) ₂ (HO) ₄ + 2 aq
6 MoO ₃ . As ₂ O ₅ . Na ₂ O . 5 H ₂ O + 7 aq	Mo ₆ As ₂ O ₁₇ (NaO) ₂ (HO) ₁₀ + 7 aq

For the convenience of comparison with the corresponding compounds of tungsten, I have in writing these formulas as far as possible assumed that all the phospho-molybdic and arsenio-molybdic acids contain 12 atoms of hydroxyl, or, in the language appropriate to the old notation, are six-basic. With the material before us, we are now prepared to discuss the question of the basicity of the phospho-tungstates

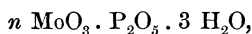
and phospho-molybdates as well as of the corresponding arsenic compounds.

The general results to which the study of the phospho-molybdates and arsenio-molybdates has led are as follows : —

1. The phospho-molybdates form a series of which the lowest term contains five atoms of molybdic to one of phosphoric oxide, and the highest twenty-four atoms of the former to one of the latter.

2. As in the case of the phospho-tungstates, the greater number of the molybdenum compounds contain an even number of atoms of tungstic oxide. The homologizing term is therefore 2 MoO_3 for these cases.

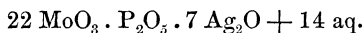
3. By far the greater number of phospho-molybdates contain *three* atoms of fixed base (old style), or, in more modern language, may be considered as derived from acids containing *six* atoms of hydroxyl. Anhydrous compounds of this type occur, and are not always simply residues obtained by heating salts which may be considered as acid, as containing, for example, $3 \text{ R}_2\text{O} \cdot 3 \text{ H}_2\text{O}$. It seems therefore necessary to admit the existence of acids of the general type



which may, however, stand in the relation of pyro-acids to other acids of the type



4. On the other hand, while no single phospho-molybdate containing more than three atoms of fixed base for one of phosphoric oxide has been obtained in a state of indubitable purity, it is probable that there is at least one salt with *six* or more atoms of fixed base. I refer to the silver salt which I have expressed by the formula

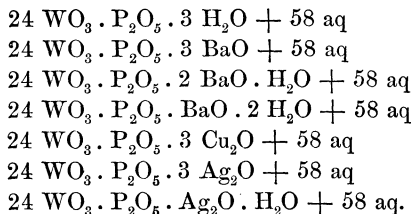


5. Setting aside the evidence derived from the analogy of the phospho-molybdates and phospho-tungstates, there is at present no sufficient proof of the existence of a series of phospho-molybdates or arsenio-molybdates containing more than *three* atoms of fixed base. Such purely negative evidence must not be too highly regarded.

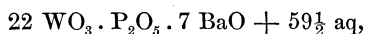
6. As in the case of the phospho-tungstates, there exists a class of phospho-molybdates in which the ratio of the number of atoms of base to that of the number of atoms of phosphoric oxide is as 5 : 2, the number of atoms of molybdic oxide being even.

Since the publication of my work on the phospho-tungstates and

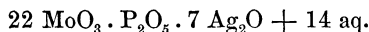
arsenio-tungstates a paper by Sprenger* on the phospho-tungstates has appeared. Sprenger has examined, with a single exception, only the compounds of the 24 : 1 series, and has added a number of new salts, which, so far as regards their constitution, fully confirm my own results. The compounds described, belonging to the 24-atom series, are the following:—



Sprenger's formula for the octahedral acid agrees with that which I had given if we consider the acid as tribasic. The other salts which he has described are new, and form a valuable addition to our knowledge of this class of compounds. It is well worthy of notice, that in all of his salts, the acid included, the number of atoms of water is the same. The acid with 58 atoms of water of crystallization forms, therefore, a complete and stable molecular structure in which 2, 4, or 6 atoms of hydrogen are replaceable. I do not recall any other series in which this constancy of crystalline water occurs, at least to the same extent. Sprenger has also obtained a salt of the 22-atom series which is of much interest. This is the barium salt



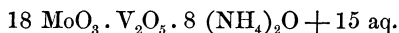
and its special interest depends upon the fact, first, that the ratio of the tungstic to the phosphoric oxide is as 22 : 1, and, secondly, that the salt contains *seven* atoms of fixed base, or, in other words, must be considered as derived from an acid containing at least *fourteen* atoms of hydroxyl. Sprenger asserts that he has obtained the corresponding acid, and it is to be hoped that he will pursue the subject farther. This barium compound furnishes additional evidence of the independent existence of a series in which the ratio is 22 : 1, and in addition it renders more probable the formula which I have given for Debray's silver salt,



From these two tolerably well-established cases it would appear that

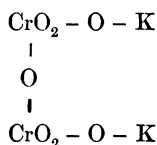
* Journal für prakt. Chemie, xxii. 418.

we are not justified in holding that the phospho-tungstates, phospho-molybdates, and corresponding arsenic compounds, have a basicity of which the higher limit is six. I may here mention that I shall hereafter describe a vanadio-molybdate of ammonium the analyses of which agree well with the formula

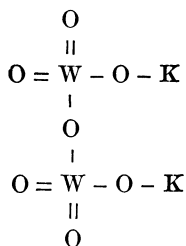


The risk of drawing hasty conclusions from purely negative evidence is particularly great in discussing the degree of basicity of this whole class of compounds, but I shall endeavor to show that it is possible to devise structural formulas which will embrace and explain all degrees of basicity which appear to be possible under the general conditions of the problem.

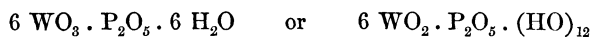
We may, as in the case of the alkaline tungstates already discussed, assume that both tungsten and molybdenum are hexatomic, and, as in that case, we may start from the commonly received formula for potassic dichromate,



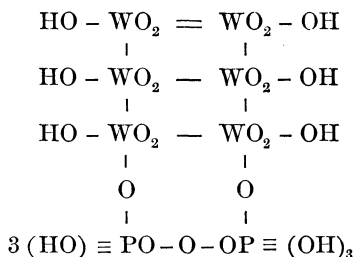
which may be equally well applied to hexatomic tungsten,



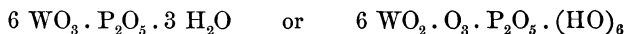
If we further suppose that the separate terms of the structural formulas are symmetrically arranged, and take a 6:1 phospho-tungstate



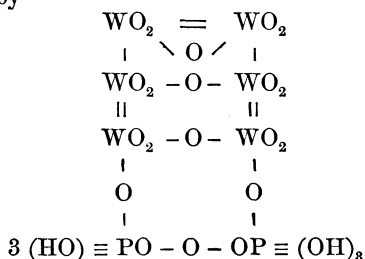
as an illustration, we may, with at least a certain degree of probability, express the structure as follows:—



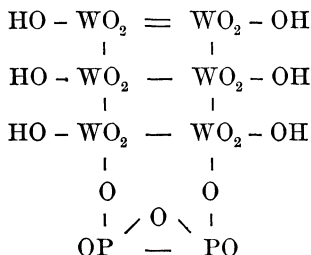
This formula explains the basicity of the acid satisfactorily. It also shows that, as six atoms of hydroxyl are united with phosphorus, and six with tungstic oxide, there should be theoretically a limiting case corresponding to an acid containing six atoms of hydroxyl, and represented by the formula



and structurally by

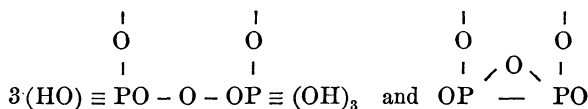


According to this view six atoms of hydroxyl are always associated with phosphorus, or, as the case may be, with arsenic. I consider this view of the subject by far the more probable. At the same time, however, it is also possible that we may have the structural formula,



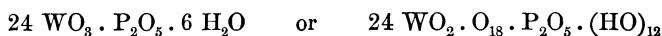
in which all the atoms of hydroxyl are associated directly with tungsten, and in the present state of our knowledge we can only decide the

question upon general grounds of probability, so that our conclusions are at best uncertain. Finally, both formulas being at least possible, it may be that there are two isomeric modifications of each series of acids represented respectively by the formulas above given. There is no present evidence of the existence of such isomeric modifications in the case of phospho-tungstates, phospho-molybdates, or the corresponding arsenic series; but Marignac has shown that there are two isomeric series of silico-tungstates, which he calls respectively silico-tungstates and tungsto-silicates, and it may be that the difference between these depends upon differences in the mode of combination, precisely similar to those which I have pointed out above. I shall return to this subject in the general discussion of my results. With respect to the two linking terms,

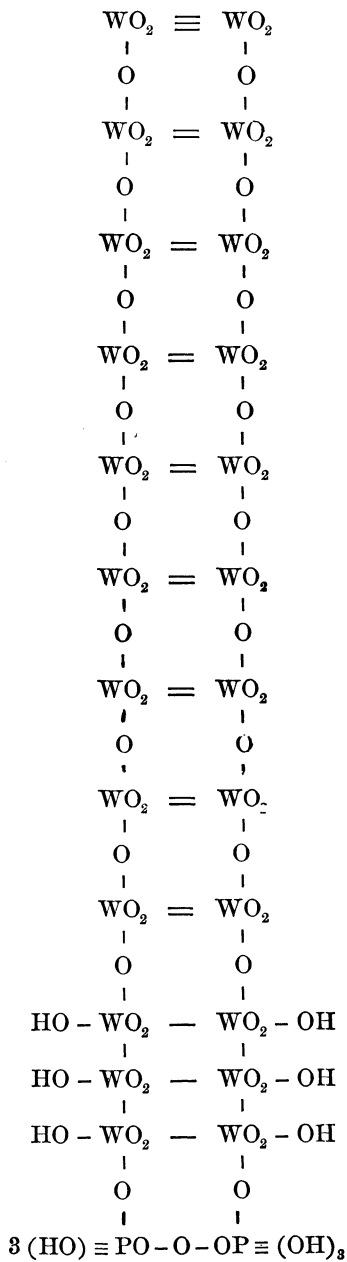


no assumption is made which is not in perfect accordance with commonly accepted views of the subject.

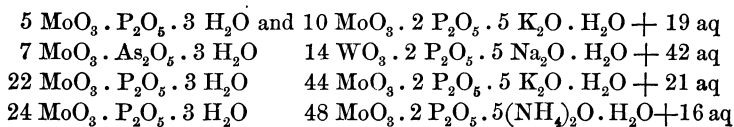
We may now consider the most general case, that, namely, in which there are twenty-four atoms of tungstic or molybdic, to one of phosphoric or arsenic oxide. We have for an acid of this type



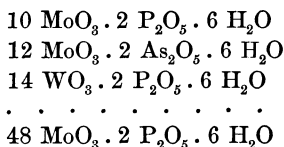
and in accordance with the principles above laid down the structural formula may be written:—



The case of an acid containing for twenty-four atoms of tungstic oxide six atoms of hydroxyl may easily be deduced from the above, upon the principle explained in the first example cited. Without again writing the cumbersome formula, it may easily be seen that the cases of acids containing more than twelve atoms of hydroxyl, if such really exist, are embraced in the above-given structural formula, and that in such cases there will be two variations in the mode of combination of the hydroxyl, similar to the two which occur when there are six or twelve atoms of hydroxyl. The structural formula given would explain simply and naturally the *tribasic* character of all known phospho-molybdates and phospho-tungstates containing twenty-four atoms of metallic oxide, since in these all the hydroxyl may be united with phosphorus exclusively, or with tungsten exclusively. It only remains to consider the case of the compounds having for one atom of phosphoric or arsenic oxide an *uneven* number of atoms of metallic oxide, as, for instance, the 5:1 and 7:1 series. In these cases also there exists, as has been shown, a second and derived series, of which the successive terms are to be regarded as formed from those of the first series by doubling the molecular weight and dropping an atom of fixed base. Thus, we have



All these salts appear to have an acid reaction. They may all be regarded as acid six-basic salts, and it is easy to see that the two series may be reduced to one by doubling the formulas of all the terms on the left, so that we shall have a single series, of which the successive terms are



This view in no wise excludes acids or salts of a higher degree of basicity. It has the advantage of bringing all the compounds together, and of being more completely in accordance with what we know of the constitution of salts belonging to simpler types. The structural formulas which I have given — provisionally, of course —

may easily be modified to suit this view, and will all be symmetrical, and suggestive of various possible isomerisms.

The study of other complex inorganic acids will, doubtless, throw further light upon the subject, and to it I shall continue to devote my leisure. It already begins to appear that inorganic compounds may possess an unexpected degree of complexity, and that very wide fields of research in inorganic chemistry are still open.

(To be continued.)